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(54) **MOLD RELEASE COMPOSITION.**

(57) A mold release composition which comprises 10-95 wt.% of a copolymer of a C<sub>1</sub>-C<sub>20</sub> polyfluoroalkyl ester of acrylic or methacrylic acid with a vinylic compound having a C<sub>8</sub>-C<sub>30</sub> alkyl group and 90-5 wt.% of a silicone. It has a sufficient ability to effect mold release, little transfers to the surface of a molding, and does not adversely affect the fabricability of the surface of a molding.

**EP 0 591 545 A1**

**BACKGROUND OF THE INVENTION**Field of the Invention

5 The present invention relates to a mold release agent composition. Particularly, it relates to a mold release agent composition for the molding, which is suitable for molding a shaped article made of a synthetic resin, a synthetic rubber or the like.

Description of Related Art

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When a shaped article made of a synthetic resin such as an acrylic resin, an epoxy resin, a urethane resin, a vinyl chloride resin, a vinyl acetate resin and a shaped article made of a synthetic rubber are shaped, a mold release agent is coated on an internal surface of a mold so as to facilitate the release of the shaped article from the mold.

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As the mold release agent used in such case, for example, wax mold release agents such as a paraffin wax, a wax of a higher fatty acid ester and a polyethylene wax are known. These wax mold release agents have been widely used, since they are available with the low cost and give the resultant shaped article having a good surface state.

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However, the wax mold release agent has low releasing strength so that sufficient release effect cannot be achieved, unless the wax mold release agent is thickly coated on the mold when the shaped article is shaped by using a material having high adhesion strength such as an epoxy resin and a urethane resin. Accordingly, the internal surface of the mold is contaminated with repeatedly conducting the molding. This problem also gives an adverse effect on the dimensional accuracy of the shaped article.

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The wax mold release agent disadvantageously has low adhesion strength to the mold so that the mold release agent easily migrates to the shaped article and has poor continuity of the release effect. This problem results in that the mold release agent must be coated each time the shaping step is to be performed.

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In addition, when the shaped article is released from the mold, a large amount of the wax mold release agent migrates to the shaped article so that the wax mold release agent gives poor fabricability (for example, printing and coating) of the shaped article surface.

As the mold release agent for solving the above problems, a fluorine-containing mold release agent [a copolymer of a polyfluoroalkyl ester of (meth)acrylic acid and a substituted vinyl compound] is known (cf. Japanese Patent Kokai Publication Nos. 101319/1984 and 255404/1985).

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Since the fluorine-containing mold release agent has excellent release strength, it gives a sufficient release effect by thinly coating it. The fluorine-containing mold release agent has better adhesion strength to the mold than the above wax mold release agent so that it gives excellent continuity of the release effect.

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However, even the fluorine-containing mold release agent cannot completely prevent the migration to the shaped article surface. The migration of the fluorine-containing mold release agent to the shaped article surface gives an adverse effect on the fabricability (printing or coating) of the shaped article surface. The reason for this is that the fluorine-containing mold release agent which migrated to the shaped article surface exhibits also the release effect against the ink and paint used for the printing and coating.

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Japanese Patent Kokoku Publication No. 8425/1991 discloses a mold release agent which comprises a copolymer obtainable by polymerizing a perfluoroalkyl group-containing vinyl monomer, a phosphoric acid-containing vinyl monomer and a hydrocarbon vinyl monomer. However, since this mold release agent contains a large amount of phosphoric acid, a curing reaction was inhibited in the case of the resin and the rubber such as a urethane resin reacting during the molding step so that the appearance of the shaped article surface is not good. In addition, the reaction of the mold release agent with the shaped article results in the contamination of the mold.

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From Japanese Patent Kokoku Publication No. 32514/1984, a mold release agent which comprises a mixture of a polyfluoroalkyl group-containing copolymer and a silicone resin is also known. However, since the silicone is mixed in a large amount, the shaped article surface is sticky and has poor fabricability. The silicone results in the pollution of the working atmosphere. The silicone-containing mold release agent has a problem that it gives a sticky shaped article surface and poor fabricability of the shaped article surface when it migrates to the shaped article surface.

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SUMMARY OF THE INVENTION

An object of the present invention is to solve the above problems and to provide a mold release agent having good fabricability of the shaped article surface and good releasability.

- 5 An aspect of the present invention resides in a mold release agent composition comprising A) 10 to 95 % by weight of a copolymer of a polyfluoroalkyl acrylate or methacrylate ester having a polyfluoroalkyl group having 1 to 20 carbon atoms and a vinyl compound having an alkyl group having 8 to 30 carbon atoms, and B) 90 to 5 % by weight of a silicone.

10 DETAILED DESCRIPTION OF THE INVENTION

When the mold release agent composition of the present invention is coated on the internal surface of the mold, both components A and B are not compatible with each other. A layer mainly containing the component A is separated from a layer mainly containing the component B, and the component A mainly plays the adhesion action to the mold and the component B mainly plays the release action from the mold. The vinyl compound having the alkyl group having 8 to 30 carbon atoms copolymerized in the component A entraps the component B due to the long chain alkyl group thereof. Namely, the layer mainly containing the component A is formed on the mold and the layer mainly containing the component B is formed on the shaped article. During the release of the shaped article, the shaped article can be easily released from the mold, since the layer mainly containing the component A does not migrate to the shaped article surface and the layer mainly containing the component B is destroyed. The amount of the layer mainly containing the component B which migrates to the shaped article after the destruction is smaller than the migration amount in the case that the mold release agent of silicone alone is used. Accordingly, the shaped article surface is not sticky and the fabricability of the shaped article surface is not adversely affected.

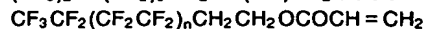
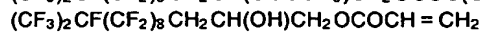
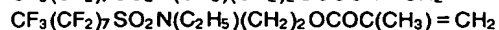
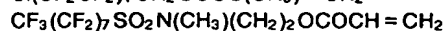
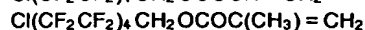
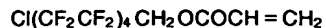
- 25 A specific example of polyfluoroalkyl acrylate or methacrylate ester preferably used in the present invention is a compound of the formula:



- 30 wherein R<sup>1</sup> is a hydrogen atom or a methyl group,  
R<sup>2</sup> is a linear or branched alkylene group having 1 to 10 carbon atoms, - SO<sub>2</sub>N(R<sup>3</sup>)R<sup>4</sup>- group or - CH<sub>2</sub>CH-(OR<sup>5</sup>)CH<sub>2</sub>- group (wherein R<sup>3</sup> is an alkyl group having 1 to 10 carbon atoms, R<sup>4</sup> is a linear or branched alkylene group having 1 to 10 carbon atoms, and R<sup>5</sup> is a hydrogen atom or an acyl group having 1 to 10 carbon atoms.), and Rf is a linear or branched polyfluoroalkyl group having 1 to 20 carbon atoms.

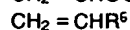
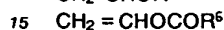
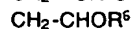
- 35 Specific examples of such compound are as follows:

- CF<sub>3</sub>(CF<sub>2</sub>)<sub>7</sub>(CH<sub>2</sub>)<sub>10</sub>OCOCH = CH<sub>2</sub>  
 CF<sub>3</sub>(CF<sub>2</sub>)<sub>7</sub>(CH<sub>2</sub>)<sub>10</sub>OCOC(CH<sub>3</sub>) = CH<sub>2</sub>  
 CF<sub>3</sub>(CF<sub>2</sub>)<sub>6</sub>CH<sub>2</sub>OCOCH = CH<sub>2</sub>  
 40 CF<sub>3</sub>(CF<sub>2</sub>)<sub>6</sub>CH<sub>2</sub>OCOC(CH<sub>3</sub>) = CH<sub>2</sub>  
 (CF<sub>3</sub>)<sub>2</sub>CF(CF<sub>2</sub>)<sub>6</sub>(CH<sub>2</sub>)<sub>2</sub>OCOCH = CH<sub>2</sub>  
 CF<sub>3</sub>(CF<sub>2</sub>)<sub>8</sub>CH<sub>2</sub>OCOCH = CH<sub>2</sub>  
 CF<sub>3</sub>(CF<sub>2</sub>)<sub>8</sub>CH<sub>2</sub>OCOC(CH<sub>3</sub>) = CH<sub>2</sub>  
 (CF<sub>3</sub>)<sub>2</sub>CF(CF<sub>2</sub>)<sub>8</sub>(CH<sub>2</sub>)<sub>2</sub>OCOCH = CH<sub>2</sub>  
 45 (CF<sub>3</sub>)<sub>2</sub>CF(CF<sub>2</sub>)<sub>10</sub>(CH<sub>2</sub>)<sub>2</sub>OCOCH = CH<sub>2</sub>  
 (CF<sub>3</sub>)<sub>2</sub>CF(CF<sub>2</sub>)<sub>6</sub>(CH<sub>2</sub>)<sub>2</sub>OCOC(CH<sub>3</sub>) = CH<sub>2</sub>  
 (CF<sub>3</sub>)<sub>2</sub>CF(CF<sub>2</sub>)<sub>8</sub>(CH<sub>2</sub>)<sub>2</sub>OCOC(CH<sub>3</sub>) = CH<sub>2</sub>  
 (CF<sub>3</sub>)<sub>2</sub>CF(CF<sub>2</sub>)<sub>10</sub>(CH<sub>2</sub>)<sub>2</sub>OCO(CH<sub>3</sub>) = CH<sub>2</sub>  
 CF<sub>3</sub>CF<sub>2</sub>(CF<sub>2</sub>)<sub>6</sub>(CH<sub>2</sub>)<sub>2</sub>OCOCH = CH<sub>2</sub>  
 50 CF<sub>3</sub>CF<sub>2</sub>(CF<sub>2</sub>)<sub>8</sub>(CH<sub>2</sub>)<sub>2</sub>OCOCH = CH<sub>2</sub>  
 CF<sub>3</sub>CF<sub>2</sub>(CF<sub>2</sub>)<sub>10</sub>(CH<sub>2</sub>)<sub>2</sub>OCOCH = CH<sub>2</sub>  
 CF<sub>3</sub>CF<sub>2</sub>(CF<sub>2</sub>)<sub>6</sub>(CH<sub>2</sub>)<sub>2</sub>OCOC(CH<sub>3</sub>) = CH<sub>2</sub>  
 CF<sub>3</sub>CF<sub>2</sub>(CF<sub>2</sub>)<sub>8</sub>(CH<sub>2</sub>)<sub>2</sub>OCOC(CH<sub>3</sub>) = CH<sub>2</sub>  
 CF<sub>3</sub>CF<sub>2</sub>(CF<sub>2</sub>)<sub>10</sub>(CH<sub>2</sub>)<sub>2</sub>OCOC(CH<sub>3</sub>) = CH<sub>2</sub>  
 55 H(CF<sub>2</sub>)<sub>8</sub>CH<sub>2</sub>OCOC(CH<sub>3</sub>) = CH<sub>2</sub>  
 H(CF<sub>2</sub>)<sub>8</sub>CH<sub>2</sub>OCOCH = CH<sub>2</sub>  
 Cl(CF<sub>2</sub>CF<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>OCOCH = CH<sub>2</sub>  
 Cl(CF<sub>2</sub>CF<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>OCOC(CH<sub>3</sub>) = CH<sub>2</sub>



(a mixture of compounds in which the values of n are 3 to 5)

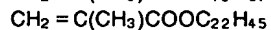
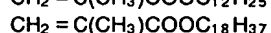
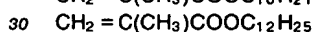
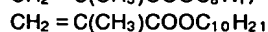
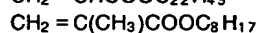
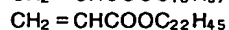
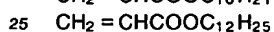
- 10 Specific examples of the preferable vinyl compound having the alkyl group having 8 to 30 carbon atoms are compounds of the formulas:



wherein R<sup>1</sup> is the same as defined above, and

- R<sup>6</sup> is an C<sub>8-30</sub> alkyl group, aralkyl group, alkenyl group, or alkyl group, aralkyl group or alkenyl group substituted with a hydroxyl group or carboxyl group.

Specific examples of such compounds are as follows:



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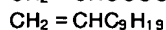
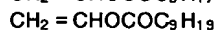
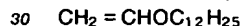
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40 The amount of the polyfluoroalkyl acrylate or methacrylate ester is preferably from 20 to 85 % by weight, more preferably from 30 to 70 % by weight of the copolymer. If it is smaller than 20 % by weight, sufficient effect cannot be obtained and the mold is often contaminated. If it is larger than 85 % by weight, the releasability is not good.

45 The carbon number of the polyfluoroalkyl group is from 1 to 20, preferably from 5 to 20, more preferably from 8 to 20. The carbon number larger than 20 is economically unsuitable.

The carbon number of the alkyl group in the vinyl compound having the alkyl group is from 8 to 30, preferably 14 to 30. If it is smaller than 8, the releasability is not sufficient, the strength of the copolymer for entrapping the silicone is low and a large amount of the silicone migrates to the shaped article so that the fabricability is deteriorated. If it is larger than 30, the vinyl compound is difficultly available and is

50 commercially unsuitable.

The copolymer may comprise other vinyl compound, for example, butyl methacrylate, ethyl methacrylate, glycidyl methacrylate, 2-hydroxyethyl methacrylate, styrene and cyclohexyl methacrylate in addition to the polyfluoroalkyl acrylate or methacrylate ester and the vinyl compound having the alkyl group having 8 to 30 carbon atoms in order to improve the film formability of the coating and the durability. The

55 amount of the other vinyl compound is preferably not larger than 10 % by weight of the copolymer. If it is larger than 10 % by weight, the releasability is deteriorated.

The copolymer according to the present invention can be prepared by any of various polymerization reaction types and conditions. Any of various polymerization reaction types such as a bulk polymerization a

solution polymerization, a suspension polymerization an emulsion polymerization and a radiation polymerization can be used.

Specific examples of the silicone used according to the present invention are a dimethylpolysiloxane oil, an alkylmethylpolysiloxane oil, a silicone resin comprising  $\text{SiO}_2$  and  $(\text{CH}_3)_3\text{SiO}_{1/2}$ .

In the mold release agent composition according to the present invention, a ratio of the copolymer to the silicone is such that the copolymer is from 10 to 95 % by weight and the silicone is from 90 to 5 % by weight, preferably the copolymer is from 10 to 90 % by weight and the silicone is from 90 to 10 % by weight, more preferably the copolymer is from 20 to 70 % by weight and the silicone is from 80 to 30 % by weight. In the above Japanese Patent Kokoku Publication No. 32514/1984, the amount of the polymer containing the polyfluoroalkyl group in the mold release agent composition is limited to 0.1 to 10 % by weight of the whole composition, since a large amount of the polymer gives an adverse effect on the releasability. However, in the present invention, since the polyfluoroalkyl group-containing copolymer comprises the vinyl compound having the alkyl group having 8 to 30 carbon atoms and gives no adverse effect on the releasability, the amount larger than 10 % by weight results in a smaller amount of the silicone and gives a good effect on the fabricability and stickiness of the shaped article surface.

When the mold release agent composition according to the present invention is coated on the mold, any of various coating procedures such as a brushing, a dip coating and a spray coating can be used. The mold release agent composition according to the present invention is preferably solved or dispersed in water or an organic solvent, when it is coated on the mold. After the coating, the drying alone is necessary. The composition may be an aerosol comprising a propellant such as 1,1,1,2-tetrafluoroethane and a liquefied petroleum gas.

The mold release agent composition according to the present invention has good solubility in various solvents. In particular, when the copolymer comprising at least 15 % by weight of the vinyl compound having the alkyl group having 8 to 30 carbon atoms is used, the composition which conventionally dissolved in only a fluorine- or chlorine-containing organic solvent or a hydrocarbon organic solvent can dissolve also in an organic solvent such as an ester organic solvent and a petroleum organic solvent so that the used solvent can be selected from an extended range of solvents. The concentration of the mold release agent composition in water or the organic solvent is generally from 0.001 to 20 % by weight, preferably from 0.01 to 3 % by weight.

#### PREFERRED EMBODIMENT OF THE INVENTION

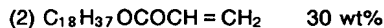
The present invention will be illustrated by the following Examples.

##### Example 1

Copolymer:



(a mixture of the compounds in which the values of n are 3, 4 and 5 in a weight ratio of 5:3:1)



A mold release agent composition consisting of the copolymer having the above composition (3 parts by weight), silicone a (0.5 parts by weight), silicone b (0.5 parts by weight) and isooctane (96 parts by weight) was subjected to a mold release test. The results shown in Table 3 were obtained. Further, in order to evaluate the fabricability of a shaped article surface, a coating test of the shaped article was conducted. The results are shown in Table 3.

##### Examples 2 to 15

Mold release agent compositions shown in Table 1 were subjected to the mold release test and the coating test. The results are shown in Table 3.

Comparative Examples 1 to 14

Mold release agent compositions shown in Table 2 were subjected to the mold release test and the coating test. The results are shown in Table 3.

## [Mold release test]

(1) A mold release agent was brush-coated on an aluminum mold having a dimension of 6 cm (diameter) x 1 cm.

(2) A urethane having the following composition was sufficiently stirred in a mixer and poured into the mold described in (1).

(3) After the urethane was cured at a room temperature for 10 minutes, the releasability was evaluated by pulling a stick which was previously stood in a shaped article.

1: The shaped article can be released from the mold almost without a force.

2: The shaped article can be released from the mold with a slight force.

3: The shaped article can be released from the mold with a strong force.

4: The shaped article cannot be released from the mold.

## [Coating test (Check pattern test)]

A coating test was conducted according to JIS D-0202.

(1) The following primer paint was brush-coated on the shaped article released in the mold release test.

(2) After the shaped article was dried at 80 °C for 10 minutes, a check pattern test was conducted.

(3) Further, the following top coat paint was brush-coated on the shaped article.

(4) After the shaped article was dried at 100 °C for 40 minutes, the check pattern test was conducted.

Composition of urethane

Polyether polyol having a hydroxyl value of 28.1 100 pbw

Ethylene glycol 19 pbw

Trichlorofluoromethane 5 pbw

Amine catalyst 0.9 pbw

Dibutyltin dilaurate 0.025 pbw

Diphenylmethanediisocyanate 104 pbw

Paint (manufactured by Dainippon Paint Co. Ltd.)

## Primer paint

Puranito L # 75 100 pbw

Puranito L # 75 Thinner 100 pbw

## Top coat paint

Puranito S 100 pbw

Puranito Thinner # 10 100 pbw

Table 1

Example No.	Copolymer Composition of copolymer	Silicone		Emulsifier		Solvent	
		pbw	pbw	pbw	pbw	pbw	pbw
1	$\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OCOCH}=\text{CH}_2$ 70wt% (a mixture of compounds wherein the values of n are 3, 4 and 5 in a weight ratio of 5:3:1) $\text{C}_{18}\text{H}_{37}\text{OCOCH}=\text{CH}_2$ 30wt%	3	Silicone a 0.5 Silicone b 0.5	—	—	Isooctane	96
2	$\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_3\text{CH}_2\text{CH}_2\text{OCOCH}=\text{CH}_2$ 30wt% $\text{C}_{18}\text{H}_{37}\text{OCOCH}=\text{CH}_2$ 70wt%	2	Silicone a 2	—	—	Decane	96
3	$\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_5\text{SO}_2\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OCOC}(\text{CH}_3)=\text{CH}_2$ 50wt% $\text{C}_{12}\text{H}_{25}\text{OCOCH}=\text{CH}_2$ 50wt%	3.5	Silicone c 0.5	—	—	Butyl acetate	96
4	$\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}(\text{OCOCH}_3)\text{CH}_2\text{OCOCH}=\text{CH}_2$ 80wt% $\text{C}_{22}\text{H}_{45}\text{OCOCH}=\text{CH}_2$ 20wt%	0.5	Silicone d 3.5	—	—	Trichloro-trifluoro-ethane	96
5	$\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_3\text{CH}_2\text{CH}_2\text{OCOC}(\text{CH}_3)=\text{CH}_2$ 85wt% $\text{C}_{10}\text{H}_{21}\text{OCOCH}=\text{CH}_2$ 15wt%	3	Silicone b 1	—	—	Trichloro-trifluoro-ethane	96
6	$\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_3\text{CH}_2\text{CH}_2\text{OCOC}(\text{CH}_3)=\text{CH}_2$ 80wt% $\text{C}_{18}\text{H}_{37}\text{OCOC}(\text{CH}_3)=\text{CH}_2$ 20wt%	1	Silicone d 3	—	—	Trichloro-trifluoro-ethane	96
7	$\text{H}(\text{CF}_2\text{CF}_2)_4\text{CH}_2\text{OCOCH}=\text{CH}_2$ 50wt% $\text{C}_{22}\text{H}_{45}\text{OCOC}(\text{CH}_3)=\text{CH}_2$ 50wt%	3	Silicone b 1	—	—	Petroleum ether	96
8	$(\text{CF}_3)_2\text{CF}(\text{CF}_2\text{CF}_2)_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{OCOCH}=\text{CH}_2$ 30wt% $\text{C}_8\text{H}_{17}\text{OCOC}(\text{CH}_3)=\text{CH}_2$ 70wt%	3	Silicone b 1	—	—	Trichloro-trifluoro-ethane	96
9	$\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_3(\text{CH}_2)_{10}\text{OCOCH}=\text{CH}_2$ 30wt% $\text{C}_{18}\text{H}_{37}\text{OCOCH}=\text{CH}_2$ 70wt%	3	Silicone b 1	—	—	Xylene	96
10	the same as in Example 1	0.5	Silicone b 0.1	—	—	Isooctane	99.4



Table 1 (continued)

Example No.	Copolymer Composition of copolymer	Silicone		Emulsifier		Solvent	
		pbw	pbw	pbw	pbw	pbw	pbw
1 1	$\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_3\text{CH}_2\text{CH}_2\text{OCOCH}=\text{CH}_2$ $(\text{HO})_2\text{P}(\text{O})\text{OCH}_2\text{CH}_2\text{OCOCH}=\text{CH}_2$ $\text{C}_{10}\text{H}_{21}\text{OCOCH}=\text{CH}_2$	50wt% 5wt% 45wt%	3		—	Trichloro- trifluoro- ethane Isopropyl alcohol	86 10
1 2	the same as in Example 1		3	Silicone a Silicone b	$\text{C}_8\text{H}_{17}-\text{O}-(\text{OC}_2\text{H}_4)_2\text{OH}$	Water	95.8
1 3	the same as in Example 2		2	Silicone a Silicone b	$\text{C}_8\text{H}_{17}-\text{O}-(\text{OC}_2\text{H}_4)_2\text{OH}$	Water	95.8
1 4	the same as in Example 1		3	Silicone a Silicone b	$\text{C}_7\text{H}_{15}\text{CO}_2\text{NH}_4$	Water	95.97
1 5	the same as in Example 2		2	Silicone a Silicone b	$\text{C}_7\text{H}_{15}\text{CO}_2\text{NH}_4$	Water	95.97

Table 2


Example No.	Copolymer Composition of copolymer	Silicone		Emulsifier		Solvent	
		Type	pbw	Type	pbw	Type	pbw
Com. 1	$\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OCOCH}=\text{CH}_2$ (a mixture of compounds wherein the values of n are 3, 4 and 5 in a weight ratio of 5:3:1)	—	4	—	—	Trichloro-trifluoroethane	96
Com. 2	$\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OCOCH}=\text{CH}_2$ $\text{C}_{18}\text{H}_{37}\text{OCOCH}=\text{CH}_2$	—	4	—	—	Trichloro-trifluoroethane	96
Com. 3	the same as in Example 1	Silicone b	3.9	—	—	Isooctane	96
Com. 4	the same as in Example 1	Silicone b	0.2	—	—	Isooctane	96
Com. 5	$\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OCOCH}=\text{CH}_2$ (a mixture of compounds wherein the values of n are 3, 4 and 5 in a weight ratio of 5:3:1)	Silicone b	3.0	—	—	Isooctane	96
Com. 6	$\text{C}_8\text{F}_{17}\text{CH}_2\text{CH}_2\text{OCOCH}=\text{CH}_2$ $\text{C}_6\text{H}_{13}\text{OCOCH}=\text{CH}_2$	Silicone b	3	—	—	Trichloro-trifluoroethane	96
Com. 7	$\text{C}_8\text{F}_{17}\text{SO}_2\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OCOCH}=\text{CH}_2$ $\text{C}_{18}\text{H}_{37}\text{OCOCH}=\text{CH}_2$	Silicone b	2.0	—	—	Trichloro-trifluoroethane	96
Com. 8	$\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_3\text{CH}_2\text{CH}_2\text{OCOCH}=\text{CH}_2$ 	Silicone b	3.0	—	—	Trichloro-trifluoroethane	96

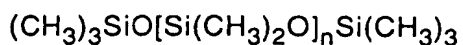
Table 2 (continued)

Example No.	Copolymer		Silicone		Emulsifier		Solvent	
	Composition of copolymer	pbw	Type	pbw		pbw	Type	pbw
Com. 9	$C_8F_{17}SO_2N(C_3H_7)CH_2CH_2OCOCH=CH_2$ $(HO)_2P(O)OCH_2CH_2OCOCH=CH_2$	50wt% 30wt%	—	4	—		Trichloro- trifluoro- ethane	86
	$C_{18}H_{37}OOCOC(CH_3)=CH_2$	20wt%					Isopropyl alcohol	10
Com. 10	the same as in Comparative Example 9	9	Silicone b	2	—		Trichloro- trifluoro- ethane	91
							Isopropyl alcohol	5
Com. 11	$C_8F_{17}SO_2N(C_3H_7)CH_2CH_2OCOCH=CH_2$ $(HO)_2P(O)OCH_2CH_2OCOCH=CH_2$	65wt% 15wt%	Silicone a	2	—		Trichloro- trifluoro- ethane	86
	$C_{18}H_{37}OOCOC(CH_3)=CH_2$	20wt%					Isopropyl alcohol	10
Com. 12	$(CF_3)_2CF(CF_2)_6(CH_2)_3OCOCH=CH_2$ $C_2H_5OCOCH=CH_2$ $CH_3COCH_2C(CH_3)NCOCH=CH_2$	73wt% 25wt% 2wt%	Silicone a	1.6	—		Methylene chloride	96
Com. 13	the same as in Comparative Example 1	1	—	4	$C_8F_{17}-\text{O}-(OC_2H_4)_2-OH$	0.2	Water	95.8
Com. 14	the same as in Comparative Example 2	2	—	4	$C_7F_{15}CO_2NH_4$	0.03	Water	95.97

Note)

Silicone a: A silicone resin which comprises  $(\text{CH}_3)_3\text{SiO}_{1/2}$  and  $\text{SiO}_2$  in a mole ratio of 2:1 and has a molecular weight of about 1,000.

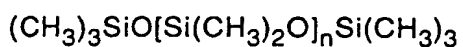
Silicone b: A silicone oil of the formula:



having a dynamic viscosity of 350 cSt.

Silicone c: A silicone resin which comprises  $(\text{CH}_3)_3\text{SiO}_{1/2}$  and  $\text{SiO}_2$  in a mole ratio of 3:2 and has a molecular weight of about 2,000.

Silicone d: A silicone oil of the formula:



having a dynamic viscosity of 1,000 cSt.

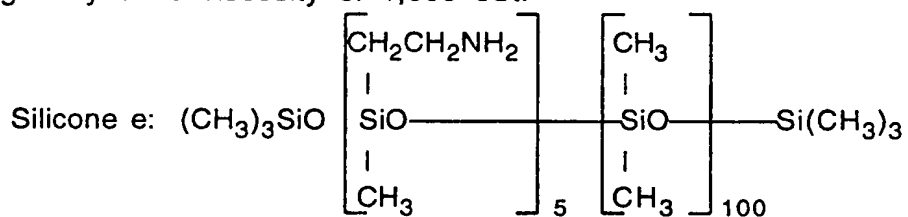


Table 3

		Mold release test	Coating test (Check pattern test)	
		Releasability	Primer	Top coat
Example	1	1	100/100	100/100
	2	1	100/100	100/100
	3	1	100/100	100/100
	4	1	90/100	90/100
	5	1	100/100	100/100
	6	1	90/100	90/100
	7	1	100/100	100/100
	8	1	100/100	100/100
	9	1	100/100	100/100
	10	2	100/100	100/100
	11	2	100/100	100/100
	12	1	100/100	100/100
	13	1	100/100	100/100
	14	1	100/100	100/100
	15	1	100/100	100/100
Com. Ex.	1	1	50/100	50/100
	2	1	50/100	50/100
	3	1	50/100	50/100
	4	2	0/100	0/100
	5	3	100/100	100/100
	6	2	50/100	50/100
	7	1	50/100	50/100
	8	3	50/100	50/100
	9	3	50/100	50/100
	10	3	80/100	80/100
	11	3	80/100	80/100
	12	2	0/100	0/100
	13	1	50/100	50/100
	14	1	50/100	50/100

Note) Coating test:

Left values of the data indicate the number of the squares which remained without completely peeling off from the shaped article, per the 100 (10 x 10) squares of 1 mm x 1 mm formed by cut lines reaching the substrate.

Claims

1. A mold release agent composition comprising
  - A) 10 to 95 % by weight of a copolymer of a polyfluoroalkyl acrylate or methacrylate ester having a polyfluoroalkyl group having 1 to 20 carbon atoms and a vinyl compound having an alkyl group having 8 to 30 carbon atoms, and
  - B) 90 to 5 % by weight of a silicone.
2. The mold release agent composition according to claim 1, wherein the amount of the copolymer is from 20 to 70 % by weight and the amount of the silicone is from 80 to 30 % by weight.
3. The mold release agent composition according to claim 1 or 2, wherein the copolymer comprises 20 to 85 % by weight of the polyfluoroalkyl acrylate or methacrylate ester having the polyfluoroalkyl group having 1 to 20 carbon atoms and 80 to 15 % by weight of the vinyl compound having the alkyl group having 8 to 30 carbon atoms

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP93/00366

A. CLASSIFICATION OF SUBJECT MATTER		
Int. Cl <sup>5</sup> B29C33/62		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
Int. Cl <sup>5</sup> B29C33/56-B29C33/64, C08L, C10M		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Jitsuyo Shinan Koho 1926 - 1993		
Kokai Jitsuyo Shinan Koho 1971 - 1993		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP, A, 62-275713 (Daikin Industries, Ltd.), November 30, 1987 (30. 11. 87), Example, claim & EP, A, 239108 & US, A, 5079299	1-3
A	JP, A, 60-255404 (Asahi Glass Co., Ltd.), December 17, 1985 (17. 12. 85), (Family: none)	1-3
A	JP, B2, 59-32514 (Shin-Etsu Chemical Co., Ltd.), August 9, 1984 (09. 08. 84), (Family: none)	1-3
A	JP, A, 59-101319 (Asahi Glass Co., Ltd.), June 11, 1984 (11. 06. 84), (Family: none)	1-3
A	JP, A, 59-102991 (Asahi Glass Co., Ltd.), June 14, 1984 (14. 06. 84), (Family: none)	1-3
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
<p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p>		
Date of the actual completion of the international search June 14, 1993 (14. 06. 93)		Date of mailing of the international search report July 6, 1993 (06. 07. 93)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.		Authorized officer Telephone No.